

EXAFS and DFT: Evidence for the $[\text{Tc}=\text{O}]^{2+}$ core†

Eric Breynaert,* Christine E. A. Kirschhock and André Maes

Received 7th July 2009, Accepted 4th September 2009

First published as an Advance Article on the web 14th September 2009

DOI: 10.1039/b913558h

A structure elucidation strategy combining X-ray Absorption Spectroscopy (XAS) and Density Functional Theory (DFT) is demonstrated and reveals the existence of the $[\text{Tc}=\text{O}]^{2+}$ moiety.

Technetium, an unusual element whereof only radioactive isotopes exist, is characterised by a very rich redox (−1 to +7) and coordination chemistry. Due to its importance for nuclear medicine and the considerable amount of Tc present in high level radioactive waste as a fission product from U it has been the focus of many studies for several decades.^{1–5} In the absence of stabilising ligands Tc(VII) and Tc(IV) are the main, stable oxidation states in oxygenated and reducing conditions, respectively. In spite of the research efforts invested in this element, some important gaps in the fundamental aqueous Tc chemistry remain. For example, two candidate geometries $\text{TcO}(\text{OH})_n^{2-n}(\text{aq})$ and $\text{Tc}(\text{OH})_m^{4-m}(\text{aq})$ are still considered possible as molecular configurations of Tc(IV) hydrolysis species because oxy- and hydroxy-coordination in these sparingly soluble Tc(IV) species (solubility of $\text{TcO}_2 \cdot x\text{H}_2\text{O} \leq 3 \times 10^{-8}$ M) can only be distinguished with ambiguity. Currently, the main argument for postulating $\text{Tc}=\text{O}^{2+}$ as the core of the hydrolysis series (TcX^{2+} , $\text{TcX}(\text{OH})^+$, $\text{TcX}(\text{OH})_2$ and $\text{TcX}(\text{OH})_3^-$, with X being either an oxygroup or two hydroxyls) is the observation that the charge of these species never exceeds +2, even at pH = 0.⁶ To our knowledge the existence of the $[\text{Tc}=\text{O}]^{2+}$ core has not been confirmed in either hydrolyzed Tc(IV) species or in any other Tc(IV) coordination compound.

The identification of specific chemical groups using the vast array of diffraction and spectroscopic means is a commonly achieved goal in crystalline solids.^{7–9} The extraction of complete, detailed structural information from dissolved species or amorphous solids is however still challenging. The desired information is often only available through a combination of state-of-the-art techniques without having access to a complete overview of the structural problem at hand.

In this contribution, evidence for the existence of a $[\text{Tc}=\text{O}]^{2+}$ core will be provided using an innovative strategy based on the combined use of X-ray Absorption Spectroscopy (XAS) and Density Functional methods (DFT) allowing local structure determination for crystalline, non-crystalline and solvated species in virtually all experimental conditions.

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy refers to the measurement of the X-ray absorption

coefficient μ as a function of the photon energy above the threshold of an absorption edge. Upon absorption of an X-ray photon, a photoelectron is ejected (outgoing wave) that will be backscattered by neighbouring atoms thereby producing an incoming electron wave. The oscillating EXAFS signal results from interference between outgoing and incoming waves.¹⁰ The Fourier Transform (FT) of EXAFS data yields a radial distribution function (RDF), providing an overview of the spatial arrangement of neighbouring atoms in a radius of *circa* 6 Å around the targeted atom. Structure elucidation can be achieved either by curve fitting the data with the sum of the individual waves originating from the neighbouring atoms, or by a linear combination analysis based on reference experiments and/or *ab initio* XAS data obtained from a model structure. The individual waves for the curve fitting process can be generated from theoretical or empirical scattering phase shifts and the amplitudes obtained from *ab initio* software like FEFF¹¹ or experiments on known reference compounds. While the first part of the RDF ($R + \Delta = 1–3$ Å) is usually dominated by (2-legged) single scattering (SS) events between the central atom and one neighbour, angular information can be deduced from multiple scattering (MS) events between three or more atoms. The calculation of theoretical phase shifts and amplitudes for MS events requires a detailed geometrical model of the studied compound. It will be shown that the combination of the easily obtained SS information with computational chemistry provides an excellent way to construct molecular geometries with the required detail for unknown systems.

Geometry optimizations identifying the lowest energy molecular geometry close to a specified starting structure are available for molecules consisting of almost all elements. Depending on the optimization problem, quantum mechanics, density functional theory or other methods can provide a computationally cost-effective solution with the required accuracy. In most cases experimental SS data combined with *a priori* information can be used to limit the number of possible starting geometries for the problem at hand. This is however not a prerequisite for the successful application of the proposed strategy (see S1†) as the sought geometry can be built by iteratively improving the initial structure based on SS data only. Optimization of these starting geometries by modelling and subsequent MS EXAFS analysis provides a means for structure determination of an unknown molecular species.

A Tc(III) reference compound $\text{Tc}(\text{acac})_3^0$, well-known from single crystal structure analysis, was prepared similarly to the method of Abrams *et al.*:^{12,13} 39 mg of $\text{Na}_2\text{S}_2\text{O}_4$ was added to a mixture of 4.6 mL 2.5 M NaOH, 5.5 mL ethanol, 2.8 mL β -diketone and 200 μl of 6.2×10^{-2} M $\text{NH}_4^{99}\text{TcO}_4$. After 24 h reaction at 65 °C the $\text{Tc}(\text{acac})_3^0$ was extracted from the red solution with 4-methyl-2-pentanone (MIBK) in a glove box (N_2/H_2 95/5%; < 2 ppm O_2). To achieve the necessary Tc concentration for XAS measurements in transmission mode the extract was concentrated to 2 mL

Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit Leuven, kasteelpark arenberg 23, B-3001, Leuven, Belgium. E-mail: eric.breynaert@biv.kuleuven.be; Fax: +32 16 321998; Tel: +32 16 321598

† Electronic supplementary information (ESI) available: [S1: overview of the EXAFS data analysis and modelling algorithm], [S2 phase- and amplitude-corrected Fourier transformation of the k^2 weighted exafs spectrum], [S3: $\text{Tc}(\text{acac})_3^0$ exafs signal reconstructed with the parameters in Table 1], [S4: FEFF input files]. See DOI: 10.1039/b913558h

using a vacuum distillation apparatus at 25 °C, equipped with a liquid nitrogen cooled condensation stage. The concentrated samples were transferred to a polypropylene sample container in the glove box and subsequently sealed in two polyethylene bags, providing three distinct sample confinements. Transportation of the samples from the radiochemical laboratory to the XAS station was performed in a steel container under an N₂/H₂ (95/5%) atmosphere to avoid contact with atmospheric oxygen.

Tchnetium K-edge XAS measurements were carried out at the dedicated radiochemistry hutch of the ROBL beamline located at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) using a double crystal monochromator (DCM) equipped with two Si(111) crystals in pseudo channel-cut mode. The spectra were recorded in transmission mode scanning from 21 keV to 22.5 keV and using 3 ion-chambers to determine I0, I1 and I2. For each scan the absolute energy calibration of the DCM was validated using a Mo foil between the 2nd and 3rd ionisation chamber.

Data reduction and analysis was achieved using a combination of XAS and modelling tools including EXAFSPAK, IFEFFIT, FEFF8 and Gaussian03 (see S1†). Initial SS fitting exclusively used phase shifts and amplitudes arising from Tc-neighbour-pairs calculated with FEFF8. The obtained crude geometry was constrained in 1 or 2 coordination shells and served as a starting model for the DFT structure optimisation.‡ Geometry optimization of the model structures used in EXAFS data analysis was performed using Density Functional Theory (DFT) utilizing the unrestricted B3LYP functional implemented in Gaussian03 rev. D02 as the model chemistry. Calculations were performed based on a mixed basis set, combining the LANL2DZ effective core potential basis set for the Tc atoms with Pople's 6-31G(d) basis set for all other atoms. This choice of DFT functional and associated basis sets is known for its good results for geometry optimization of technetium compounds.¹⁴ All atoms in the optimized geometries were then used as input for FEFF8 calculations† to obtain phase shifts and amplitudes for all significant 2 to 4-legged scattering paths. Fitting results were used as the basis for a recursive geometry refinement (see S1†) until the model spectrum exhibited all major EXAFS features while exhausting all important scattering paths identified by FEFF.

Although the electronic spectrum of the samples diluted in acetonitrile did not show absorption bands§ other than those described in literature,^{12,13,15-17} the EXAFS data provided indisputable evidence for the presence of a second technetium species next to Tc(acac)₃⁰.

The asymmetric EXAFS envelope (Fig. 1), provided the initial indication for the presence of this second species. A coordination environment dominated by an almost perfect octahedral oxygen shell should not be so strongly asymmetric. A second, strong indication was the presence of two maxima in the imaginary part under the nearest neighbour signal in the RDF after phase-and amplitude-corrected FT of the *k*³ weighted EXAFS spectrum (see S2†). In the case of the octahedral coordination of Tc in the Tc(acac)₃⁰ complex, the symmetric first shell of oxygen atoms would result in one single peak with a symmetrical imaginary part, having its maximum at the top of the absolute magnitude and at the correct coordination distance.¹⁸

When assuming the presence of a second Tc species next to the Tc(acac)₃⁰ (± 70%) the experimental spectrum could be reproduced with high accuracy (Fig. 1, Fig. 2, Table 1). Table 2 demonstrates

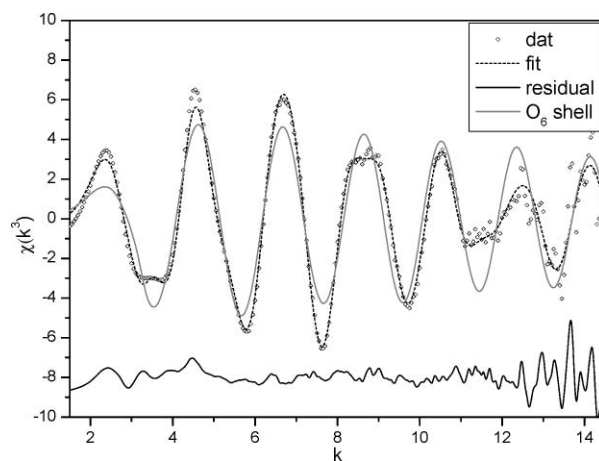


Fig. 1 *k*³ weighted EXAFS data, fit [Tc(acac)₃⁰ + Tc=O(OH)₂(H₂O)₃], residual and contribution of the 1st O-shell of Tc(acac)₃⁰ (see S3†).

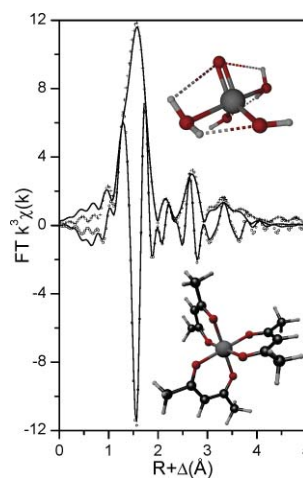


Fig. 2 Fourier transformed EXAFS data (magnitude/imaginary part) and fit.

the excellent agreement between the radial distances derived by EXAFS for the Tc(acac)₃⁰ complex with crystallographic and DFT optimisation† results.¹⁶

The strongest contribution of the second species to EXAFS intensity was unambiguously identified as one short (1.73 Å) oxygen bond typical for a Tc–oxo bond. Based on the recursive fitting algorithm (see S1†), either a distorted octahedral 6-coordinate TcO(OH)₂(H₂O)₃ species or a highly symmetric 5-coordinated trigonal bipyramidal TcO(OH)₂(H₂O)₂ species can account for the EXAFS pattern. The presence of any acac ligands in this species could clearly be excluded.

In the presence of only oxo, hydroxo and aquo ligands Tc(III) is highly unstable and is readily oxidised to Tc(IV). In addition, the observed intermediate edge energy (max 1st derivative: 21056.3 eV, −6.4 eV vs. TcO₄[−]) and the absence of any pre-edge features also point to a mixture of Tc(III) and Tc(IV) Tc species.¹⁹⁻²¹ A loss of acac ligands during the concentration procedure could easily lead to the oxidation of Tc(III) ions and the formation of the identified TcO(OH)₂(H₂O)_x species. Oxidation to Tc(V) can be excluded because bond distances between Tc(V) and O in [Tc=O]³⁺ species are typically much smaller (1.59 to 1.68 Å)² than those

Table 1 EXAFS fit data

Path ^a	<i>N</i>	<i>R</i>	σ^2	S_0^2	<i>R</i> -factor ^b
Tc ₁ -O	6	2.030	0.00136	$S_0^2(\text{Tc}_1)^d$	0.2631
Tc ₁ -C ₁	6	2.964	0.00212		0.2298
Tc ₁ -C ₂	3	3.318	0.00188		0.2187
Tc ₁ -O-Tc ₁ -O	6	4.097	0.00271		0.1491
Tc ₁ -C ₁ -O	12	3.098	0.008 ^c		0.0794
Tc ₂ -O ₁	1	1.728	$\sigma^2(\text{Tc}_1\text{-O})$	$S_0^2(\text{Tc}_2)^d$	0.0317
Tc ₂ -O ₂	2	1.966			
Tc ₂ -O ₃	2	2.198			
Tc ₂ -O ₄	1	2.511			
Tc ₁ -C ₃	6	4.396	0.004 ^c	$S_0^2(\text{Tc}_1)^d$	0.0304
Tc ₁ -C ₃ -O	12	4.430	0.01292		0.0284
Tc ₁ -O-C ₃ -O	6	4.415	0.00892		
Tc ₁ -C ₁ -C ₃ -O	12	4.503	0.01441		
$S_0^2(\text{Tc}_1)$	0.6135		$\Delta E_0(\text{Tc}_1)$	-1.557	
$S_0^2(\text{Tc}_2)$	0.3865		$\Delta E_0(\text{Tc}_2)$	-3.828	

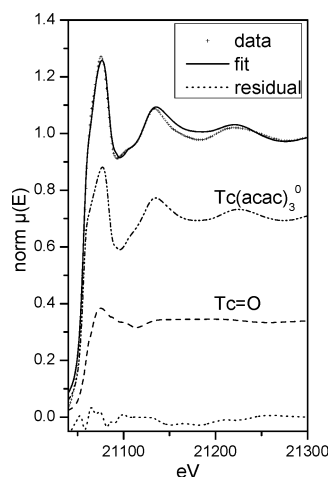
^a Tc₁: Tc(acac)₃⁰; Tc₂: TcO(OH)₂(H₂O)₃. ^b *R* factor is shown for each path added to the fit, all other parameters show the final fit values. During the fit procedure, additional paths were fitted in order of appearance until the *R* factor was not further reduced. ^c fixed. ^d $S_0^2(\text{Tc}_1) = 1 - S_0^2(\text{Tc}_2)$.

Table 2 Comparison of EXAFS fitted distances (Å) for Tc(acac)₃⁰ with DFT and XRD results

Path	EXAFS	DFT	XRD ¹⁶
Tc-O	2.030	2.053	2.025
Tc-C ₁	2.964	3.008	2.945
Tc-C ₂	3.318	3.380	3.295
Tc-C ₃	4.396	4.359	4.296

derived here. Therefore we conclude that the new species contains Tc(IV).

The DFT optimized geometries[‡] obtained by the recursive EXAFS fitting algorithm (see S2[†]) were used as input for *ab initio* full multiple scattering calculation of their XANES spectra using the mixed Dirac-Hara/Hedin Lundqvist exchange correlation potential implemented in FEFF8 (see S4[†]). Fig. 3 shows the excellent agreement between the experimental XANES spectrum and a linear combination fit of the *ab initio* spectra for the

**Fig. 3** XANES data, fit, residual and FEFF8 generated LC components Tc(acac)₃⁰ and TcO(OH)₂(H₂O)₃.

two Tc species in solution (Athena; weight: 0.71/0.328; ΔE^0 : 0.467/-2.030 respectively).

The described recursive geometry refinement methodology based on the combined use of XAS and computational chemistry (DFT, FEFF) (see S1[†]) was previously undocumented and allowed for the first time to indisputably identify the ‘oxy’ coordination in the molecular structure of a Tc(IV) hydrolysis species TcO(OH)₂(H₂O)_x present as an impurity in a Tc(acac)₃⁰ reference solution.

Acknowledgements

The authors would like to thank the ROBL beamline scientists and especially Dr. A. Rossberg, Dr. A. Scheinost, Dr. C. Hennig and Dr. H. Funke for their excellent user support during the XAS measurements. E.B. thanks KULeuven for financial support and acknowledges a fellowship as Postdoctoraal Onderzoeker van het Fonds Wetenschappelijk Onderzoek-Vlaanderen. CEAK acknowledges support by the Flemish Funds for Scientific Research (FWO Vlaanderen), and long-term structural Methusalem funding by the Flemish Government. Research was conducted utilizing high performance computational resources provided by the University of Leuven, <http://ludit.kuleuven.be/hpc>

Notes and references

- [‡] Gaussian03, rev. D.02²² ub3lyp/lanl2dz[Tc]/6-31G(d)[[C,H,O]]
[§] UV-VIS bands; exp. (Shimadzu UV-1650 PC): 531, 503, 377, 348, 285, 274 nm; literature: 535, 505, 375, 348, 283, 270//533, 505, 372, 347, 283, 272 nm.^{12,13,15-17}
- J. A. Rard, M. H. Rand, G. Anderegg, and H. Wanner, *Chemical Thermodynamics of Technetium*, Elsevier Science B.V., Amsterdam, 1999.
 - K. Schwochau, *Technetium: chemistry and radiopharmaceutical applications*, Wiley-VCH, Weinheim; Chichester, 2000.
 - E. Breynaert and A. Maes, *Anal. Chem.*, 2005, **77**, 5048–5054.
 - A. Maes, K. Geraedts, C. Bruggeman, J. Vancluysen, A. Roßberg and H. Hennig, *Environ. Sci. Technol.*, 2004, **38**, 2044–2051.
 - K. Geraedts and A. Maes, *Appl. Geochem.*, 2008, **23**, 1127–1139.
 - J. A. Rard, *J. Nucl. Radiochem. Sci.*, 2005, **6**, 197–204.
 - G. Gauglitz, and T. Vo-Dinh, *Handbook of Spectroscopy*, Wiley-VCH Verlag GmbH & Co. KGaA, 2003.
 - W. P. Jensen, G. J. Palenik and I. H. Suh, *J. Chem. Educ.*, 2003, **80**, 753–761.
 - C. Brundel, Richard, C. A. J. Evans, and S. Wilson, *Encyclopedia of Materials Characterization - Surfaces, Interfaces, Thin Films*, Elsevier, 1992.
 - B. K. Teo, *EXAFS: basic principles and data analysis*, Springer-Verlag, Berlin, New York, 1986.
 - A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **58**, 7565.
 - M. J. Abrams, A. Davison, A. G. Jones and C. E. Costello, *Inorg. Chim. Acta*, 1983, **77**, L235–L236.
 - K. Leesmeister and K. Schwochau, *Nucl. Med. Biol.*, 1992, **19**, 73–78.
 - J. Gancheff, C. Kremer, E. Kremer and O. N. Ventura, *THEOCHEM*, 2002, **580**, 107–116.
 - G. S. Patterson, A. Davison, A. G. Jones, C. E. Costello and S. D. Maleknia, *Inorg. Chim. Acta*, 1986, **114**, 141–144.
 - K. Hashimoto, C. Kabuto, T. Omori and K. Yoshihara, *Chem. Lett.*, 1988, 1379–1380.
 - H. Kido and Y. Hatakeyama, *Inorg. Chem.*, 1988, **27**, 3623–3625.
 - D. C. Koningsberger, B. L. Mojet, G. E. van Dorssen and D. E. Ramaker, *Top. Catal.*, 2000, **10**, 143–155.
 - I. Almahamid, J. C. Bryan, J. J. Bucher, A. K. Burrell, N. M. Edelstein, E. A. Hudson, N. Kaltsoyannis, W. W. Lukens, D. K. Shuh, H. Nitsche and T. Reich, *Inorg. Chem.*, 1995, **34**, 193–198.

-
- 20 W. W. Lukens, D. K. Shuh, N. C. Schroeder and K. R. Ashley, *Environ. Sci. Technol.*, 2004, **38**, 229–233.
- 21 F. Poineau, M. Fattahi, C. Den Auwer, C. Hennig and B. Grambow, *Radiochim. Acta*, 2006, **94**, 283–289.
- 22 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN03 (Revision D.2)*, Gaussian, Inc., Wallingford, CT, 2004.